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Graft Copolymerization of Vinyl Monomers onto Modified Cottons. VIII. Dimethylaniline–Benzyl Chloride-Induced Grafting of Methyl Methacrylate onto Partially Carboxymethylated Cotton

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Synopsis

The feasibility of dimethylaniline (DMA)–benzyl chloride (BC) mixture to initiate graft polymerization of methyl methacrylate (MMA) onto partially carboxymethylated cotton was examined. The graft yield depends on the nature of the solvent used along with water; ethanol proved to be the best at a water:ethanol ratio of 90:10. Considerable grafting occurred in the presence of acetic acid at a concentration of 200 mmol/l. Higher concentrations of this acid decrease grafting significantly. The graft yield obtained in the presence of formic acid was much lower than that obtained in the presence of acetic acid. Inclusion of hydrochloric or sulfuric acid in the graft polymerization system prevent grafting. A DMA–BC mixture at a concentration of 0.08:0.087 mole/l. constitutes the optimal concentration for grafting. This contrasts with 0.32:0.35 mole/l. for total conversion. The rate of grafting increases by raising the polymerization temperature; it follows the order 50° > 60° > 65° > 70° > 75°C. Furthermore, increasing the monomer concentration caused a significant enhancement in the graft yield and total conversion.

INTRODUCTION

During the last few years, chemically modified celluloses have evoked considerable interest in the grafting area. Indeed, vinyl graft polymerization onto modified celluloses has proved of value to arrive at a good understanding of the kinetics and mechanisms of grafting as well as to obtain basic information needed for improvements to be made in the properties of the products.[1–12]

Previous reports have dealt with vinyl graft polymerization onto cellulose xanthate using H_2O_2 as initiator,[1] phosphorylated cellulose using Fe^{2+}–H_2O_2 redox systems,[2] and cyanoethylated cellulose using either irradiation[3] or the ceric ion method for initiation.[4] The ceric ion method has also been used for grafting vinyl monomers onto partially carboxymethylated cellulose,[5] acrylamidomethylated cellulose,[6] acetylated cellulose,[7] carbamoylethylated cellulose,[6] crosslinked cellulose,[8] oxidized cellulose,[9] and cellulose bearing sulfur-containing groups,[10] carboxyethyl together with cyanoethyl groups[6] or carboxymethyl along with cyanoethyl groups.[6] In addition, potassium permanganate[11] and azobisisobutyronitrile[12] have been reported to initiate vinyl graft polymerization onto modified celluloses.

In this work, partial carboxymethylation of cellulose was performed prior to

grafting. The chemically modified cellulose so obtained was subjected to graft copolymerization with methyl methacrylate (MMA) in the presence of dimethylaniline–benzyl chloride–acetic acid mixture as initiator to see the feasibility of this system for initiating grafting.

EXPERIMENTAL

Partially carboxymethylated cotton having 11 meq COOH/100 g cellulose was prepared by a method of Kamel et al.[13] using 12*N* sodium hydroxide and 2*N* sodium chloroacetate. MMA was washed successively with 5% NaOH and water, then dried with anhydrous sodium sulfate, and distilled under reduced pressure in nitrogen before use. Dimethylaniline (Merck) free from monoethylaniline was distilled under vacuum in nitrogen atmosphere. The colorless product was preserved under nitrogen in a dark bottle. Benzyl chloride (Merck) was freshly distilled under reduced pressure. The solvents ethanol, *n*-propanol, isopropanol, *n*-butanol, *tert*-butanol, dimethyl sulfoxide (DMS), dimethylformamide (DMF), dioxane, and acetic, formic, sulfuric, and hydrochloric acids were pure-grade chemicals.

The graft polymerization reaction was carried out as follows: A conditioned PCMC sample (1 g) was introduced in a 70-ml glass-stoppered Erlenmayer flask containing 50 ml of a solution consisting of water, solvent, DMA, BC, acid, and MMA at a specific temperature. The flasks were immediately stoppered and kept in a thermostat for different periods from 30 to 240 min. The entire operation was conducted in atmospheric oxygen. During the reaction, the PCMC was kept well immersed in the solution. The fibers were then removed, thoroughly washed, repeatedly Soxhleted with acetone, and dried to constant weight.

The percentage graft yield and percentage total conversion were calculated from the following equations:

$$\% \text{ graft yield} = \frac{\text{wt. of grafted polymer}}{\text{dry wt. of PCMC sample}} \times 100$$

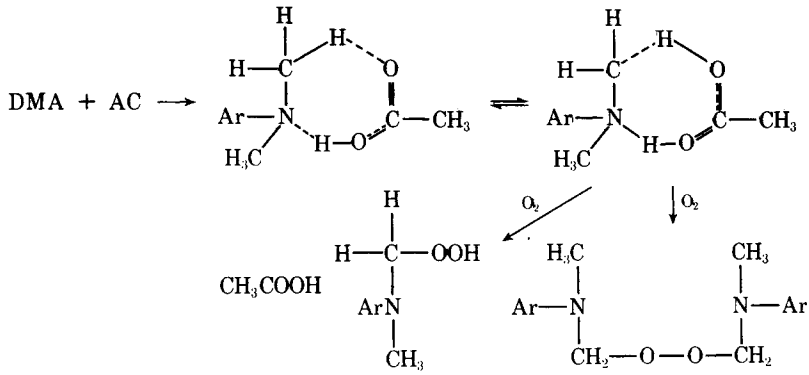
$$\% \text{ total conversion} = \frac{\text{wt. of grafted polymer + wt. of homopolymer}}{\text{wt. of monomer used}} \times 100$$

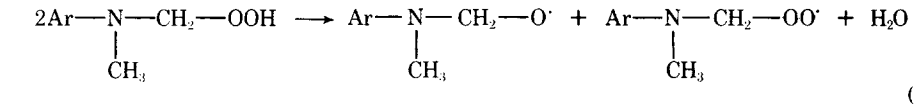
RESULTS AND DISCUSSION

Mechanism

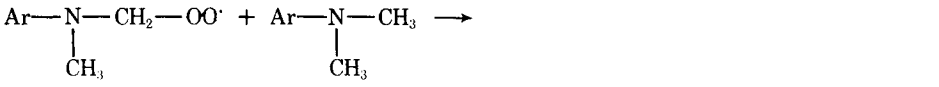
The initiating capability of DMA/BC in the presence of acetic acid (AC) to induce vinyl polymerization has been described to follow different paths.[14–17] Accordingly, a tentative reaction mechanism has recently been elicited for vinyl graft polymerization using this system as shown below.[18]

1. AC accelerates the auto-oxidation of DMA, via hydrogen-bonded complex formation, to yield aminohydroperoxide which functions as chain carrier in the following auto-oxidation:





(1)



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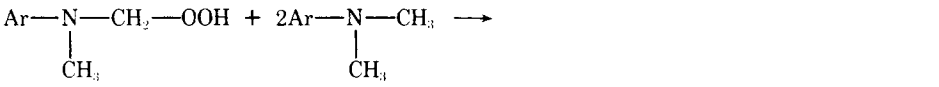

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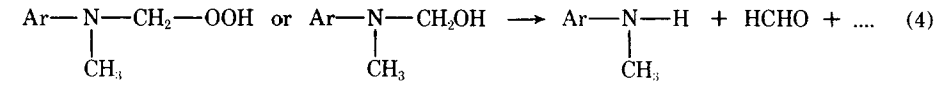

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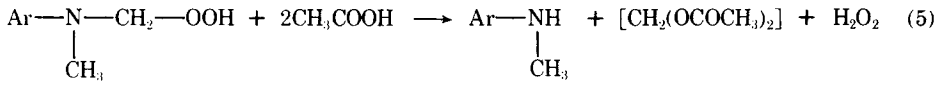

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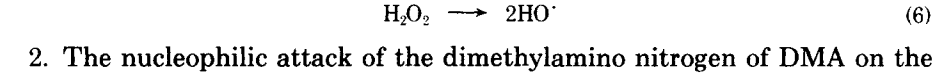
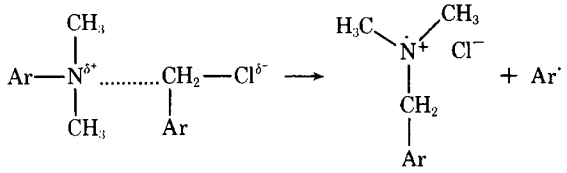


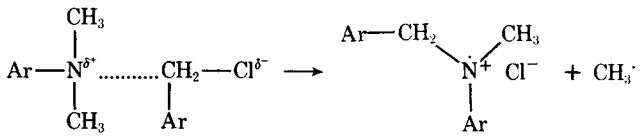
(6)

2. The nucleophilic attack of the dimethylamino nitrogen of DMA on the methylene carbon in BC gives rise to generation of free radicals as suggested by eq. (7):



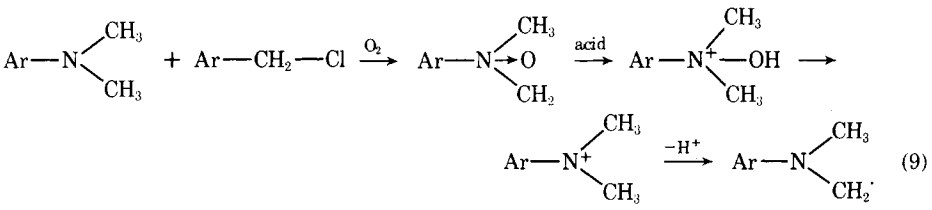
(7)

3. Alkyl exchange of the aniline occurred upon reacting DMA with BC and creation of methyl radicals as suggested by eq. (8):



(8)

4. Formation of dimethylaniline N-oxide is possible in the presence of atmospheric oxygen and benzyl chloride. This oxide can undergo further fission, thereby producing free radicals as suggested by eq. (9):



(9)

If the free radicals suggested by eqs. (1)–(3) and (6)–(9) are capable of abstracting hydrogen atoms from the hydroxyl groups of PCMC, macroradicals of the latter will be formed. In the presence of monomer, grafting would be initiated via addition of these free radicals to the double bonds of the monomer molecules. Indeed, this is found to be true as is seen from the results presented below.

Polymerization Medium

Table I shows the graft yield obtained when polymerization of MMA onto PCMC was carried out in various media using DMA–BC–AC mixture as initiator. It is clear that grafting increases considerably as the ratio of water in the solvent:water mixture increases. Within the range studied and regardless of the solvent used, a solvent:water mixture of 10:90 constitutes the most favorable reaction medium. However, the nature of the solvent does affect the magnitude of grafting. For a given solvent:water ratio, the graft yield follows the order

ethanol > DMF > *n*-propanol > isopropanol >dioxane
> *n*-butanol > *tert*-butanol.

It is understandable that the higher graft yield found with media having greater ratio of water in the solvent:water mixture is due to the ability of water to swell PCMC thereby accentuating diffusion of monomer and initiator into fibers. Furthermore, hydrogen and/or hydroxyl radicals may be formed under the in-

TABLE I
Effect of Solvent:Water Ratio on Graft Polymerisation[a]

Solvent type	Graft Yield, %			
	10:90[b]	25:75	50:50	75:25
Ethanol	100	94	86	79
n-Propanol	48	42	30	28
Isopropanol	43	38	30	26
n-Butanol	38	32	26	24
tert-Butanol	34	28	23	20
Dimethylformamide	52	46	35	32
Dioxane	42	35	28	26

[a] [DMA]:[BC], 0.08:0.087 mole/l.; MMA, 8%; reaction time, 4 hr; temperature, 70°C; PCMC:liquor ratio, 1:50.
[b] Solvent:water ratio.

fluence of the primary radical species of the initiating system on water.[19] Thus, besides the primary radical species, these hydrogen and hydroxyl radicals may be involved in graft initiation.

The dependence of grafting upon the nature of the solvent suggests that the solvents examined differ considerably in their (a) capability of swelling PCMC, (b) miscibility with monomer, (c) formation of solvent radical from the primary radical species of the initiating system, (d) contribution of the solvent radical in activation of PCMC, and (e) termination of the graft radical and PCMC macroradical via chain transfer. While the first four factors favor grafting by simplifying access and diffusion of monomer, the last factor adversely affects grafting by lowering the molecular size of the graft.[20,21]

Effect of Acids

Addition of acetic acid to the DMA–BC initiating system has been reported to accelerate the rate of vinyl polymerization.[14] Inclusion of acids in the grafting reaction has also been disclosed to have a significant influence on the magnitude of grafting, depending on the kind and amount of acid used.[11,12]

In Table II are shown the graft yields obtained in the presence of either acetic acid, formic acid, sulfuric acid, or hydrochloric acid at different concentrations. As is evident, presence of acetic acid at a concentration of 200 mmole/l. in the polymerization medium brings about a graft yield of 100%. This is dropped sharply by increasing the acetic acid concentration to a value of 10% at a concentration of 800 mmole/l. The same trend is obtained with formic acid, but the graft yield is much lower and the decrease in grafting by increasing the acid concentration is not so significant as in case of acetic acid. The presence of sulfuric acid or hydrochloric acid, on the other hand, offsets the reaction and no grafting occurs.

The higher graft yields obtained in the presence of acetic acid at lower concentrations could be associated with its ability to speed up the auto-oxidation of DMA, via hydrogen-bonded complex formation, to yield aminohydroperoxides which function as chain carriers in the auto-oxidation.[20] The decreased grafting at higher acetic acid concentration could be accounted for by the possibility of salt formation of aniline derivatives with lower initiating activity.[16,23]

The lower grafting found with formic acid than acetic acid suggests that formic acid provides hydrogen ions which act as terminators for the free radicals in the

TABLE II
Grafting of MMA onto PCMC by DMA–BC Initiator System Using Different Acids[a]

	Graft yield, %			
Acid used	200 mmole/l.[b]	400 mmole/l.	600 mmole/l.	800 mmole/l.
Acetic	100	40	22	10
Formic	20	18	16	13
Sulfuric	C	C[c]	C	C
Hydrochloric	C	C	C	C

[a] [DMA]:[BC], 0.08:0.087 mole/l.; ethanol:water, 10:90; MMA, 8%; temperature, 70°C; reaction time, 4 hr; PCMC:liquor ratio, 1:50.

[b] Concentration of acid.

[c] C, No grafting.

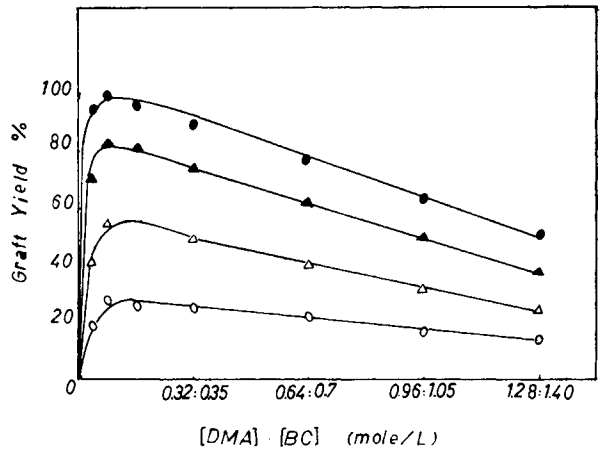


Fig. 1. Influence of initiator system concentration on graft yield: (○) 1 hr; (△) 2 hr; (▲) 3 hr; (●) 4 hr; [AC], 200 mmole/l; ethanol:water, 10:90; MMA, 8%; temperature, 70°C; PCMC:liquor ratio, 1:50.

reaction medium. Once it occurred, it would reflect on the initiation of grafting.[24]

That no grafting has taken place in the presence of sulfuric acid or hydrochloric acid indicates that these acids are not only able to form the aniline salts with slight initiating activity,[16,23] but also provide hydrogen ions which are presumably used in the termination of free radicals in solution and on the PCMC backbone.

Initiator Concentration

The effect of the concentration of DMA–BC mixture on the graft yield is shown in Figure 1. It is clear that, for a given reaction time, increasing the initiator, i.e., DMA:BC, concentration up to 0.08:0.087 mole/l. causes a considerable enhancement in the graft yield. Beyond this concentration, a decrease in the grafting is observed. That is, a nearly equimolecular mixture of DMA and BC at a concentration of 0.08:0.087 mole/l. constitutes the optimal concentration for grafting.

The decrease in the grafting by increasing the initiator concentration could possibly be associated with a faster rate of termination probably owing to abundance of free-radical species in the polymerization system. It is also possible that at higher initiator concentration, DMA reacts with BC to yield quaternary ammonium salt which is not capable of initiating polymerization.[14] A third possibility is that homopolymerization may prevail over grafting at higher initiator concentration. There is, however, little reason to believe that one of the three possibilities is operating to the exclusion of the other, though the third possibility is substantiated by the data presented below.

Figure 2 shows the influence of initiator concentration on the total conversion. Here, too, whatever the reaction time within the range studied, the total conversion increases as the initiator concentration increases, attains a maximum, and then falls at higher concentrations, similar to grafting. But maximum total

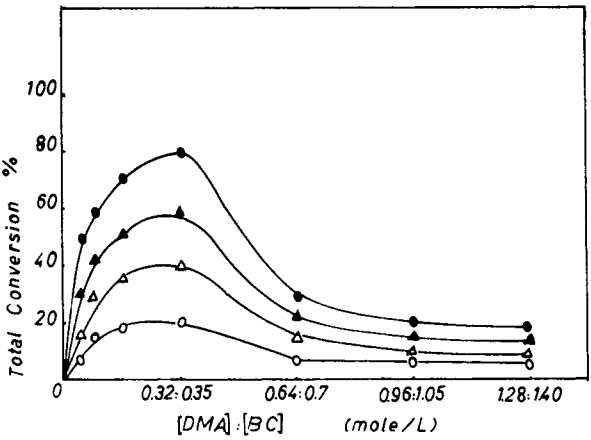


Fig. 2. Influence of initiator system concentration on total conversion: (○) 1 hr; (△) 2 hr; (▲) 3 hr; (●) 4 hr; [AC], 200 mmole/l.; ethanol:water, 10:90; MMA, 8%; temperature, 70°C; PCMC:liquor ratio, 1:50.

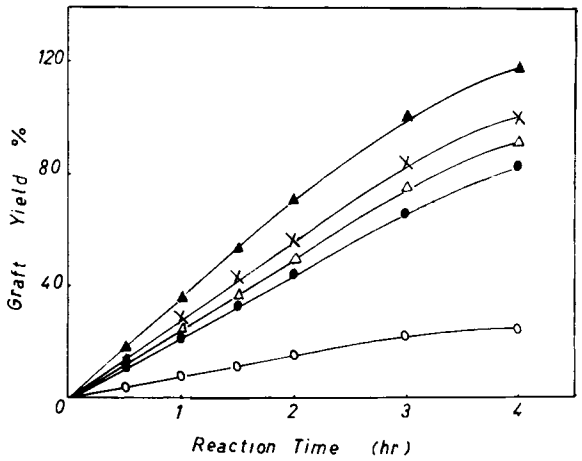


Fig. 3. Influence of MMA concentration on rate of grafting. [MMA]: (○) 2%; (●) 4%; (△) 6%; (×) 8%; (▲) 12%; [DMA]:[BC], 0.08:0.087 mole/l.; [AC], 200 mmle/l.; ethanol:water, 10:90; temperature, 70°C; PCMC:liquor ratio, 1:50.

conversion is achieved upon using a nearly equimolecular mixture of DMA–BC at a concentration of 0.32:0.35 mole/l., in contrast with 0.08:0.087 mole/l. for maximum grafting. Since the total conversion is the sum of monomer converted to graft as well as homopolymer, this finding indicates that homopolymerization is more favored than grafting at concentrations of DMA–BC mixture higher than 0.08:0.087 mole/l. This, indeed, substantiates the third possibility suggested above for explaining the fall in grafting at higher initiator concentration.

Monomer Concentration

Figure 3 shows the effect of MMA concentration on the graft yield. It is obvious that grafting is higher the higher the concentration of MMA in the poly-

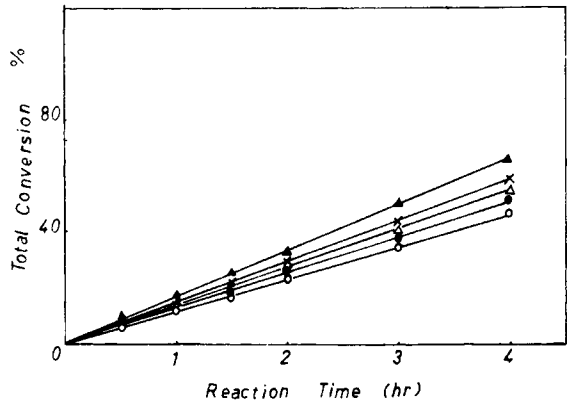


Fig. 4. Influence of MMA concentration on rate of total conversion. [MMA]: (○) 2%; (●) 4%; (△) 6%; (×) 8%; (▲) 12%; [DMA]:[BC], 0.08:0.087 mole/l.; [AC], 200 mmole/l.; ethanol:water, 10:90; temperature 70°C; PCMC:liquor ratio, 1:50.

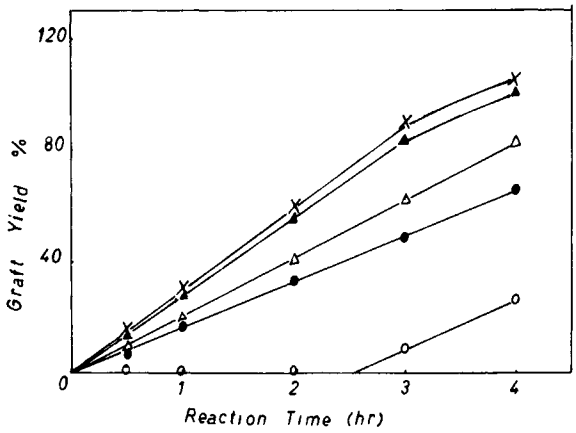


Fig. 5. Effect of temperature on rate of grafting: (○) 50°C; (●) 60°C; (△) 65°C; (▲) 70°C; (×) 75°C; [DMA]:[BC]:[AC], 0.08:0.087:200 mmole/l.; ethanol:water, 10:90; [MMA], 8%, PCMC:liquor ratio, 1:50.

merization system. The same situation is also encountered with respect to the total conversion (cf. Fig. 4). At higher concentration of MMA, the gel effect[24] brought about by the solubility of poly(methyl methacrylate) in its own monomer seems to be more pronounced. As a result, termination of the growing grafted chain radicals by coupling is hindered while the swellability of PCMC is enhanced. The ultimate effect of this is increased grafting.

Besides the gel effect, complex formation between PCMC and MMA is more favorable at higher concentration of MMA. Complexation of PCMC with MMA activates the latter through formation of a donor–acceptor complex in which the uncomplexed MMA, though normally an electron acceptor, behaves as a donor relative to the complexed MMA, which has been converted to a stronger acceptor. Enhanced monomer reactivity is also apparently due to association of complexed monomer into organized array, since PCMC acts as a matrix for such alignment. Naturally, the effect of the enhanced monomer reactivity is increased grafting.

A similar assumption has been reported for grafting cellulose,[11,12,25] wool,[18,26,27] and nylon[24] with MMA using different initiators.

Reaction Temperature

The effect of polymerization temperature on the rate of grafting is shown in Figure 5. At 50°C, the grafting reaction is accompanied by a long induction period (150 min), whereas at a temperature of 60°C or higher, the reaction proceeds without any induction period. The rate of grafting also increases by increasing the temperature up to 70°C. Above this temperature, the increment in the rate of grafting is not so striking.

The enhancement in grafting by raising the polymerization temperature suggests that the latter performs the following functions: (a) increasing the concentration of active species, i.e., free radicals, in the polymerization system; (b) accentuating the swelling properties of PCMC; (c) improving the solubility of MMA; (d) accelerating diffusion of MMA from the polymerization medium to PCMC; and (e) enhancing the rate of initiation and propagation of the graft. There is no doubt that all these functions give rise to higher grafting.

Reaction Time

The effect of increasing the polymerization time is to bring about a significant enhancement in the graft yield (Figs. 1, 3, and 5). The same holds true for total conversion (Figs. 2 and 4). However, the magnitude of this enhancement is governed by the polymerization temperature, monomer concentration, as well as initiator concentration.

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